Report 108-M6

INVESTIGATION OF ZEOLITE MEMBRANES FOR FUEL CELLS

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1.0 INTRODUCTION AND SUMMARY

Experimental work has continued in the development and evaluation of inorganic membranes for hydrogen-oxygen fuel cell application. It was determined that the drying time and temperature range for producing inorganic membranes having favorable conductivity and strength characteristics was somewhat narrower than anticipated. Accordingly, the statistical plan for optimizing membrane composition and preparation techniques has been revised to reduce drying temperatures and drying time-temperature ranges.

The significant effect of drying conditions on sintered membrane strength are discussed and the results of preparing a membrane composition without oven drying are reported. It was found that elimination of the drying operation increased membrane strength after sintering by more than 50% for a membrane made from 40% C.P. ZrO_2, 20% H_3PO_4, and 40% "Zeolon H."

Electrical conductivity measurements for four different compositions are reported. It was found that the use of calcia stabilized zirconia in place of C.P. zirconia produced membranes having favorable low resistivities. Since the use of calcia stabilized zirconia also produced high membrane strength, these findings are very encouraging from the point of view of producing high strength inorganic membranes which will operate satisfactorily in fuel cells. The conductivity data obtained from the three other compositions evaluated confirmed the previous observation that reduced drying temperatures resulted in improved electrical characteristics for a given membrane composition.

A re-examination of fuel cell design and assembly techniques resulted in elimination of erratic cell operation and improved cell performance. It was also found that one membrane composition (1 zirconium phosphate : 1 H_3PO_4 : 1 "Zeolon H") improved in performance as the temperature was increased.

2.0 EXPERIMENTAL WORK AND DISCUSSION

2.1 Membrane Composition Studies

During the month a number of the compositions, outlined in the statistical plan for optimizing composition and preparation techniques for membranes, were prepared and tested. Although a review of the work previously reported indicated that there was a fairly wide range of compositions and drying conditions which would produce phosphate-bonded inorganic membranes having favorable conductivity and strength characteristics, it was found that these ranges were narrower than anticipated. If drying temperatures were too high the membranes produced had low strength after sintering and if drying temperatures were too low, the membrane material was too "wet" to granulate and compact satisfactorily into membrane form. The problem was further complicated by the fact that compositions containing large amounts of phosphoric acid or "Zeolon H" require longer drying times and higher drying temperatures to permit granulation and compaction. As a result, it was necessary to revise the composition and drying time-temperature ranges outlined in the statistical plan. In general, drying temperatures and phosphoric acid content were reduced and the range of drying temperatures to be investigated was narrowed based upon these findings. The revised plan of experiments is shown in Table 1. All of the

compositions contain 30% ZrO_2, drying conditions range from 20 to 60 hours between 140°C and 160°C and the phosphoric acid content varies between 16% and 30%.

Approximately 75% of the treatments shown in Table 1 were prepared during the month and are now being pressed and sintered. Modulus of rupture and electrical conductivity measurements will be made and it is anticipated that this work will be completed during the December period. These data will then be evaluated statistically in order to optimize composition and preparation techniques used in fabricating inorganic fuel cell membranes.[1]

It has been previously reported[2] that drying conditions have a significant effect on membrane characteristics. Drying at too high a temperature or for too long a period of time tends to reduce strength, while short drying times and low temperatures produce materials which are too "wet" for good granulation and uniform pressing. It is believed that a part of the bonding action which takes place between the phosphoric acid and the zirconia and "Zeolon H" occurs during drying and that this bond strength is lost when the material is subsequently granulated and pressed. The remainder of the bonding reaction between the components occurs during sintering and produces strength in the finished membrane. It seems desirable, then, to limit drying time and temperature to a minimum which will permit granulation and proper membrane compaction. This should result in the development of maximum strength during sintering for a given composition.

In a discussion of these findings, the project officer suggested that membranes be prepared without drying in order to evaluate this theory. Accordingly, a composition consisting of 40% zirconia, 20% phosphoric acid and 40% "Zeolon H" was prepared by thoroughly mixing the ingredients and pressing into 2 in. diameter membranes at 15 tons total load without oven drying. The membranes were sintered for 15 hr at 500°C and their strength was measured. These membranes were strong having a modulus of rupture of 37770 ± 119 psi. When the same composition was prepared by drying for 15 hr at 160°C, pressed at 15 tons total load and sintered for 24 hr at 300°C, the strength was 2433 ± 250.[3] This increase in strength of more than 50% is substantial and much of the increase is obviously due to elimination of the drying operation.

These results show that membrane strength can be increased by eliminating the drying operation or by keeping drying time and temperature at a minimum. It also suggests vacuum drying as a means of reducing water content at low temperatures in order to develop maximum strength during membrane sintering.

2.2 Conductivity Measurements

Electrical conductivities of four different inorganic membranes were determined as a function of relative humidity at each of two different temperatures. The apparatus used in making these measurements has been described in previous reports. Resistivities are reported as the average value for three individual membranes, and the error is shown as standard deviation. The resistivities obtained for the four membrane compositions are shown in Tables 2, 3, 4, and 5. All of the compositions shown in the tables were sintered at 500°C for 15 hr. Table 2 shows the resistivity of membrane No. 191-057 which was made from a composition using stabilized zirconia* instead of C.P. ZrO_2.

*Zircoa "B" Zirconium Corporation of America, Solon, Ohio

Tables 3, 4, and 5 show the effect of varying drying time and temperature on the resistivity of membranes having the same composition.

The resistivities reported for the four membranes which were evaluated range from 75 to 170 ohm-cm at 105°C and a relative humidity of 56%. The membrane having the lowest resistivity (75 ohm-cm) was No. 191-057 in which stabilized zirconia was used in place of C. P. ZrO_2. Since this value falls within the range of membrane resistivities which have performed well in fuel cell evaluations and membranes prepared from calcia stabilized zirconia have also had excellent strength, further work with this type of zirconia is planned.

The three other membranes which were evaluated have the same chemical composition; 1 C. P. ZrO_2 : 1 H_3PO_4 : 1.3 "Zeolon H." However, drying times and temperatures were varied in order to determine the effect of drying conditions on membrane resistivity. Examination of Tables 3 and 4, shows that drying for 40 hr at 140°C compared to 40 hr at 160°C reduced resistivity from 170 ohm-cm to 97 ohm-cm at 105°C and 56% relative humidity. Increasing the drying time from 40 to 60 hr at 140°C, however, only increases the resistivity from 97 to 105 ohm-cm. These results are very encouraging as they show that high strength and low resistivity are compatible from the standpoint of drying conditions and indicates that it should not be necessary to "trade off" strength in order to obtain low resistivity membranes.

2.3 Fuel Cell Operation

Table 6 shows fuel cell operating data obtained during the period covered by this report. In order to allow the fuel cell to fulfill its primary function as a reliable analytical device for testing the comparative efficiency of various membranes, a re-examination of the fuel cell components and the procedure used in assembling them was made. This analysis showed that the cement being used to make a gas tight seal between the membrane and the teflon gasket (silicone rubber) allowed gas to escape and was the principle cause of inconsistent performance.

Accordingly, an epoxy resin was substituted for the silicone cement and the diameter of the electrodes was increased from 1.63 to 2.0 in. to match the diameter of the membrane. This made it possible to assemble these components between the steel back-up plates and cement the edges with resin in one continuous operation. The back-up plate O-ring seals were also coated with high vacuum silicone grease before final cell assembly.

The improved cell assembly has operated without failure or irregularities since it was redesigned. An example of the improved cell operation is seen with membrane 191-050. The current density at 0.5 volts increased from 24.7 ma/cm^2 (old assembly : Run #11) to 31.7 ma/cm^2 (new assembly : Run #25). These results are probably also associated with improved catalyst - membrane contact as well as the elimination of gas leakage.

Fuel cell evaluation of membranes has shown that the performance of one membrane composition (1 zirconium phosphate : 1 H_3PO_4 : 1 "Zeolon H") was not significantly affected by temperature increases in the range studied.

Figure 1 shows polarization curves for this membrane, (No. 191-050) at several temperatures using both the old and the improved assembly methods. It is interesting to note that in using the new assembly method an improvement in performance was noted as the temperature was elevated in contradistinction to what was observed in the past. Figure 2 illustrates these results graphically and shows voltage as a function of temperature at constant current density. Previous performance curves are also shown for comparative purposes.

The standardized behavior of the new assembly and the improvement of performance with temperature for a given composition is encouraging. It should be noted that other water balancing agents besides "Zeolon H" may be used, now that improved membrane formation techniques permit an extension of experimental work into other areas.

REFERENCES

1. "Investigation of Zeolite Membrane Electrolytes for Fuel Cells," NASA Contract NAS8-150, Monthly Progress Report for period ending 7 October 1963, Astropower, Incorporated, Report 108-M4, p 3.

2. "Investigation of Zeolite Membrane Electrolytes for Fuel Cells," NASA Contract NAS 7-150, Progress Report for period ending 18 March 1963 Quarterly, Astropower, Incorporated, Report 108-Q3, p 2-1 (1963).

3. "Investigation of Zeolite Membrane Electrolytes for Fuel Cells," NASA Contract NAS 7-150, Monthly Progress Report for period ending 7 November 1963, Astropower, Incorporated, Report 108-M5, p 5.

TABLE 1

REVISED STATISTICAL PLAN OF EXPERIMENTS

X_1 = Percentage of H_3PO_4
X_2 = Hours of Drying Time
X_3 = Drying Temperature in ^oC
(N = 3)

Treatments	X_1	X_2	X_3
1	23	40	160
2	23	60	150
3	23	40	150
4	27-1/6	52	144
5	23	40	150
6	18-5/6	52	156
7	30	40	150
8	23	40	150
9	23	40	150
10	18-5/6	28	144
11	27-1/6	28	156
12	23	20	150
13	18-5/6	28	156
14	23	40	150
15	27-1/6	28	144
16	18-5/6	52	144
17	27-1/6	52	156
18	16	40	150
19	23	40	140
20	23	40	150

TABLE 2

RESISTIVITIES AT TWO TEMPERATURES
(MEMBRANE NO. 191-057)

Composition: ZrO_2, H_3PO_4, "Zeolon H"
(1:1:1 parts by weight)

Processing Conditions: Drying Temperature = 160°C
Drying Time = 15 hours

Relative Humidity (%)	Resistivity (Ohm-Cm)
Temperature 89.8°C	
71	$(2.46 \pm 1.11) \times 10^2$
45	$(3.62 \pm 1.16) \times 10^2$
11	$(1.49 \pm 0.16) \times 10^5$
Temperature 105.8°C	
56	$(7.54 \pm 0.26) \times 10^1$
41	$(1.47 \pm 1.22) \times 10^2$
11	$(2.83 \pm 0.87) \times 10^3$

TABLE 3

RESISTIVITIES AT TWO TEMPERATURES
(MEMBRANE NO. 191-055)

Composition: ZrO_2, H_3PO_4, "Zeolon H"
(1:1:1.3 parts by weight)

Processing Conditions: Drying Temperature = 160°C
Drying Time = 40 hours

Relative Humidity (%)	Resistivity (Ohm-Cm)
Temperature 89.8°C	
71	$(1.68 \pm 0.67) \times 10^2$
45	$(2.06 \pm 1.20) \times 10^2$
11	$(1.56 \pm 0.13) \times 10^5$
Temperature 105.2°C	
70	$(6.79 \pm 0.96) \times 10^1$
56	$(1.70 \pm 0.72) \times 10^2$
26	$(1.85 \pm 1.15) \times 10^2$
11	$(4.99 \pm 1.22) \times 10^3$

TABLE 4

RESISTIVITIES AT TWO TEMPERATURES
(MEMBRANE No. 191-059)

Composition: ZrO_2, H_3PO_4 "Zeolon H"
(1:1:1.3 parts by weight)

Processing Conditions: Drying Temperature = 140°C
Drying Time = 40 hours

Relative Humidity (%)	Resistivity (Ohm-Cm)
Temperature 89.8°C	
71	$(1.66 \pm 0.06) \times 10^2$
45	$(6.22 \pm 3.99) \times 10^2$
11	$(1.78 \pm 0.62) \times 10^5$
Temperature 105.4°C	
56	$(9.66 \pm 0.58) \times 10^1$
26	$(3.25 \pm 0.47) \times 10^2$
11	$(2.50 \pm 0.74) \times 10^3$

TABLE 5

RESISTIVITIES AT TWO TEMPERATURES
(MEMBRANE NO. 191-058)

Composition: ZrO_2, H_3PO_4, "Zeolon H" (1:1:1.3)

Processing Conditions: Drying Temperature = 140°C
Drying Time = 60 hours

Relative Humidity (%)	Resistivity (Ohm-Cm)
Temperature 89.8°C	
71	$(2.34 \pm 0.73) \times 10^2$
45	$(5.14 \pm 2.28) \times 10^2$
11	$(1.45 \pm 0.29) \times 10^5$
Temperature 105.4°C	
56	$(1.05 \pm 0.26) \times 10^2$
26	$(1.02 \pm 0.73) \times 10^3$
11	$(2.27 \pm 1.13) \times 10^3$

TABLE 6

FUEL CELL DATA

Run No.	Membrane No.	Thickness Mm	Electrode Area Cm^2	Temp °C	Ma/Cm^2 at 0.5V	Slope (RxA) (Ohm-Cm^2)	Resistivity** at 100% R.H. Ohm-Cm	Observed Fuel Cell Resistance Ohms	Calculated*** Fuel Cell Resistance Ohms	Circuit Voltage Ohms
25	191-050	0.61	20.2	65	28.5	9.7	--	0.48	--	0.80
				89	31.7	8.1	27	0.40	0.39	0.78
				95	33.3	7.7	--	0.38	--	0.78
11*	191-050	1.31	13.4	90	24.7	17.4	27	1.30	1.26	1.02
26	191-032	0.72	20.2	65	29.1	16.3	145	0.81	0.83	1.06
				89	24.7	17.3	100	0.86	0.67	1.01
28	191-068	0.79	13.4	65	24.6	17.0	--	1.27	--	0.97
				89	17.5	23.0	--	1.72	--	0.98

* Report 108 M5, Table VI

** Extrapolated from conductivity data

*** Calculated from resistivity, membrane dimensions, and estimated electrode contact resistance. (0.3 ohms for 20.2 cm^2 area; 1.0 ohms for 13.4 cm^2 area). Electrode contact resistance estimate for 20.2 cm^2 area was made as described in Report 108-M5, using the resistivity ratios of membrane 191-050 in Run 25 and membrane 191-032 in Run 26.

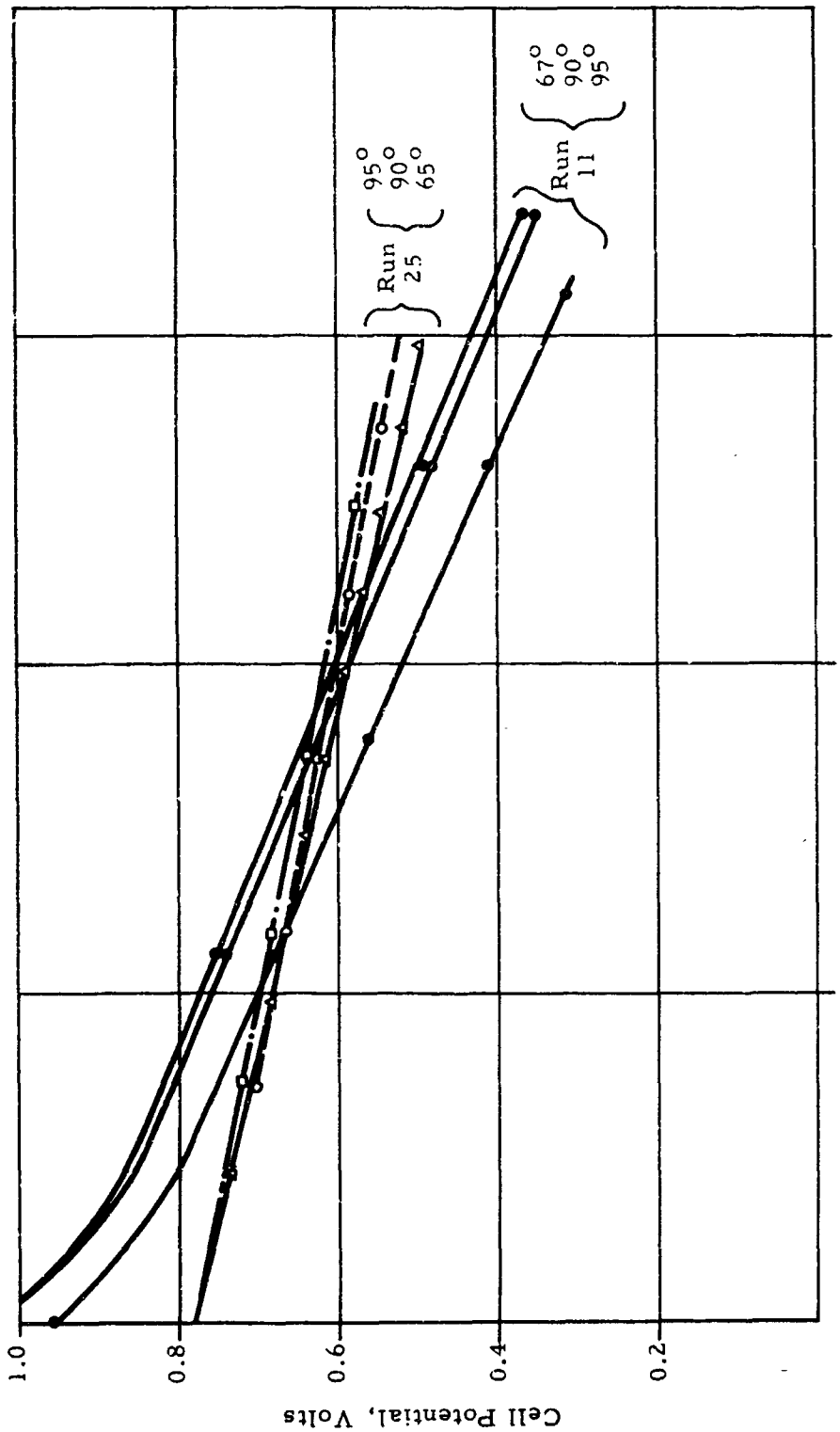

Figure 1. Polarization Curves for Membrane 191-050

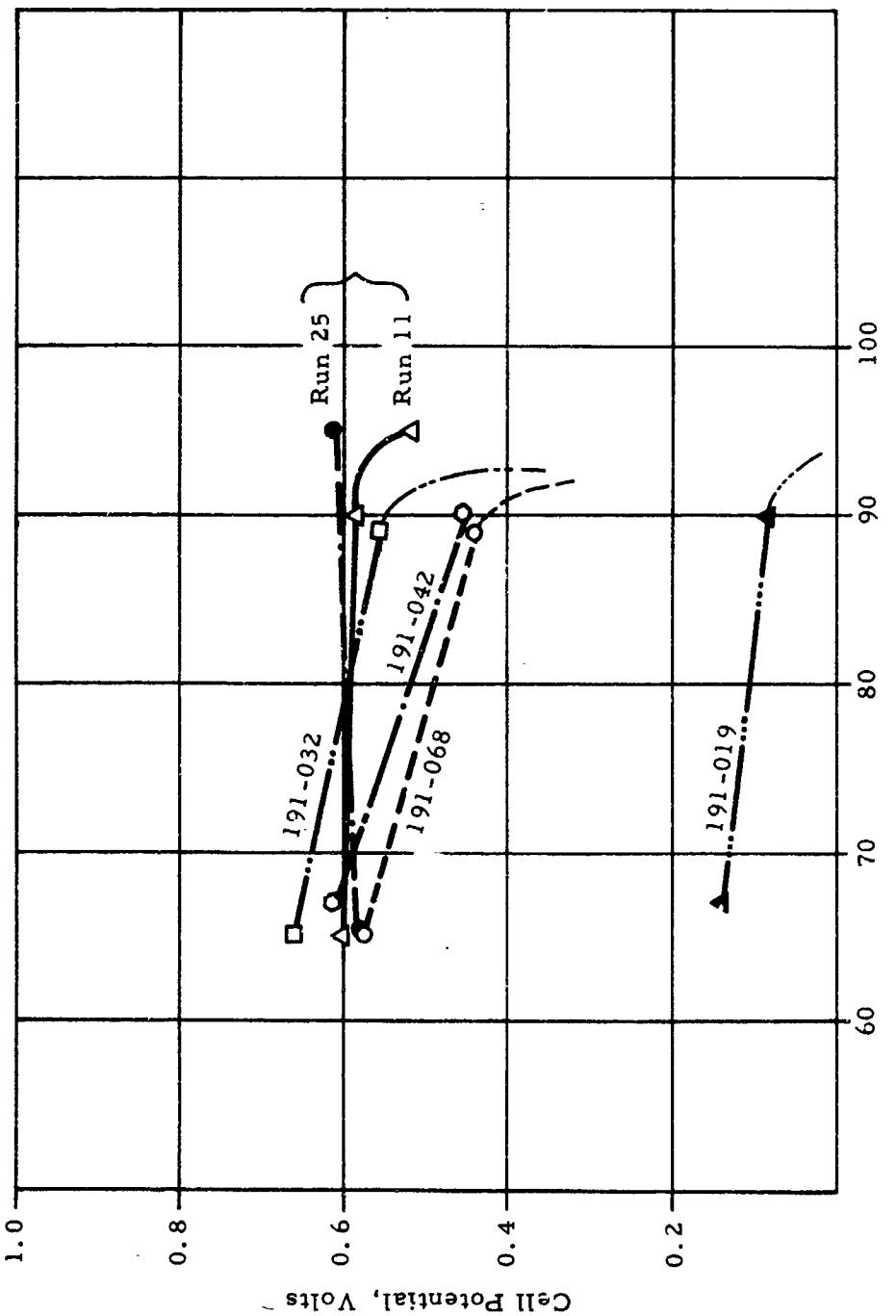

Figure 2. Cell Voltages vs Temperatures at 20 Ma/Cm^2 for Several Membranes